

Chapter 13. NMR

"for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution"

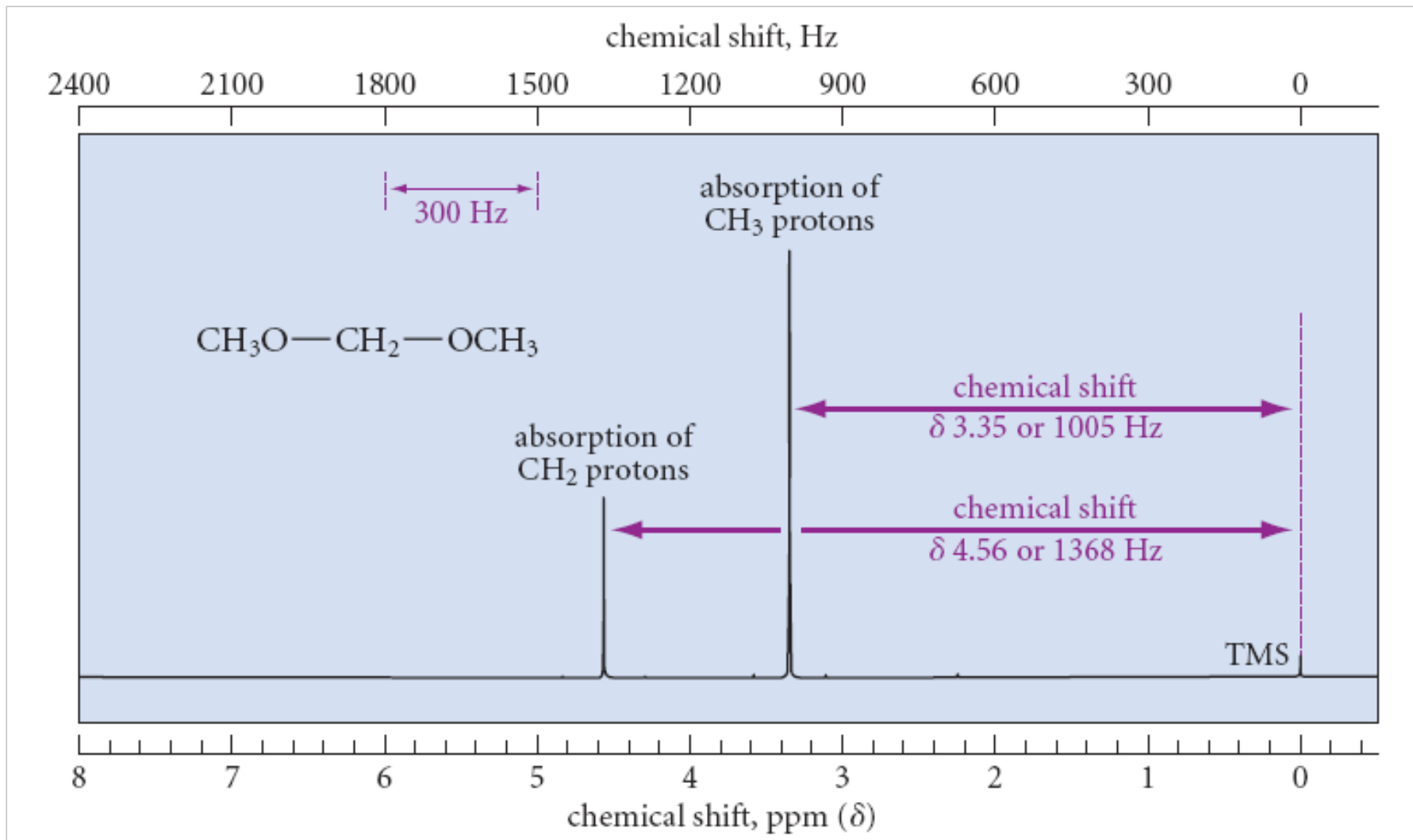


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Nuclear magnetic resonance

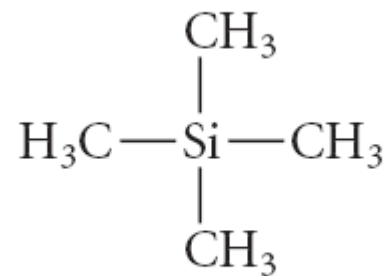


Chemical shifts

The position of an absorption on the horizontal axis is called its chemical shift.

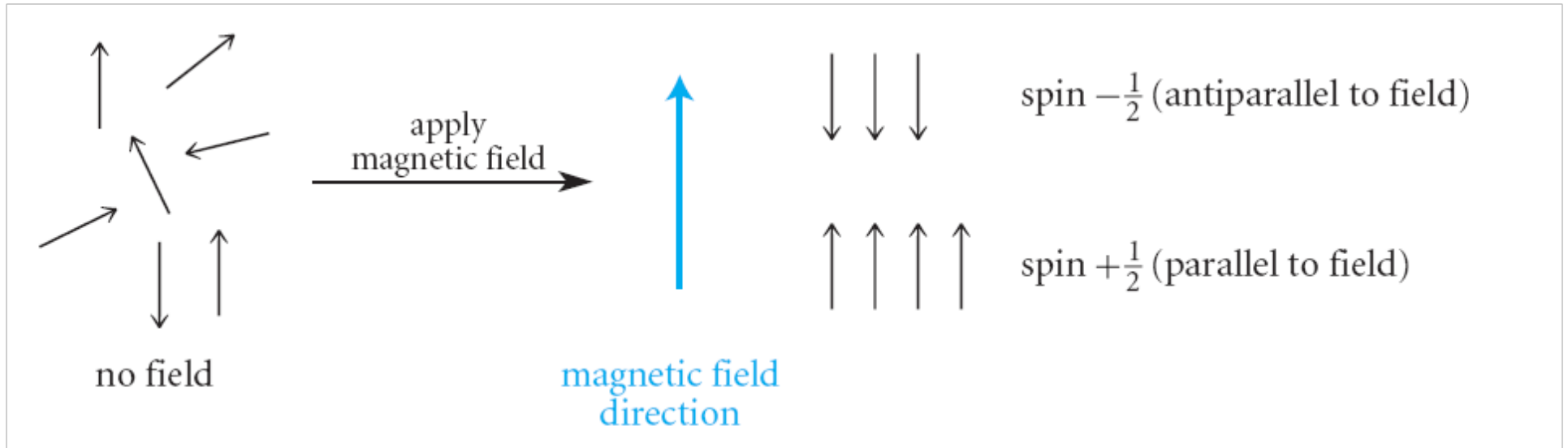
$$\delta = \frac{\Delta\nu}{\nu_0} \quad (\Delta\nu \text{ in Hz, } \nu_0 \text{ in MHz})$$

Reference: TMS



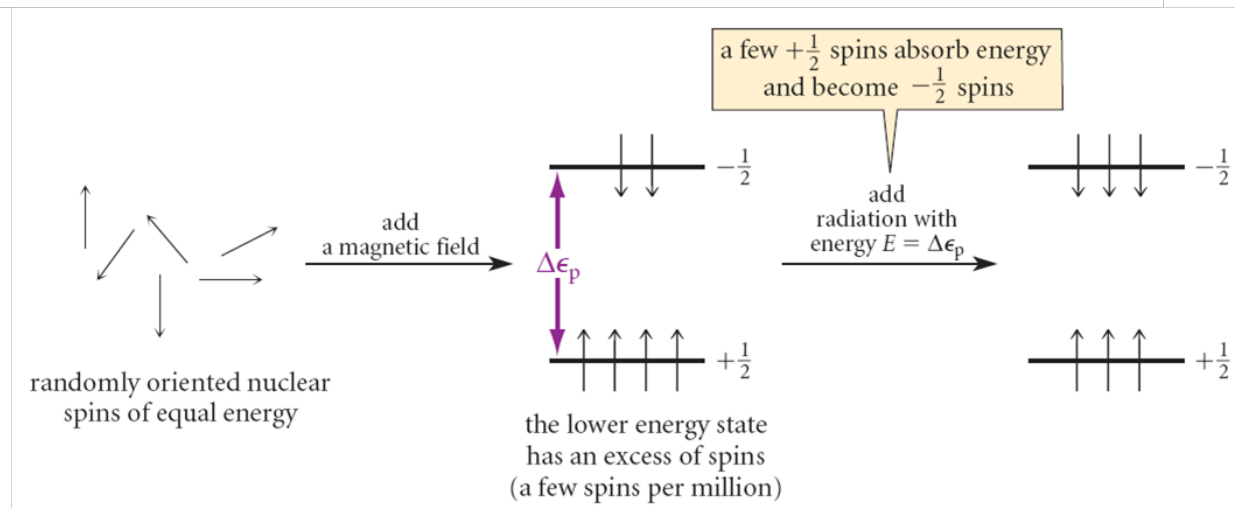
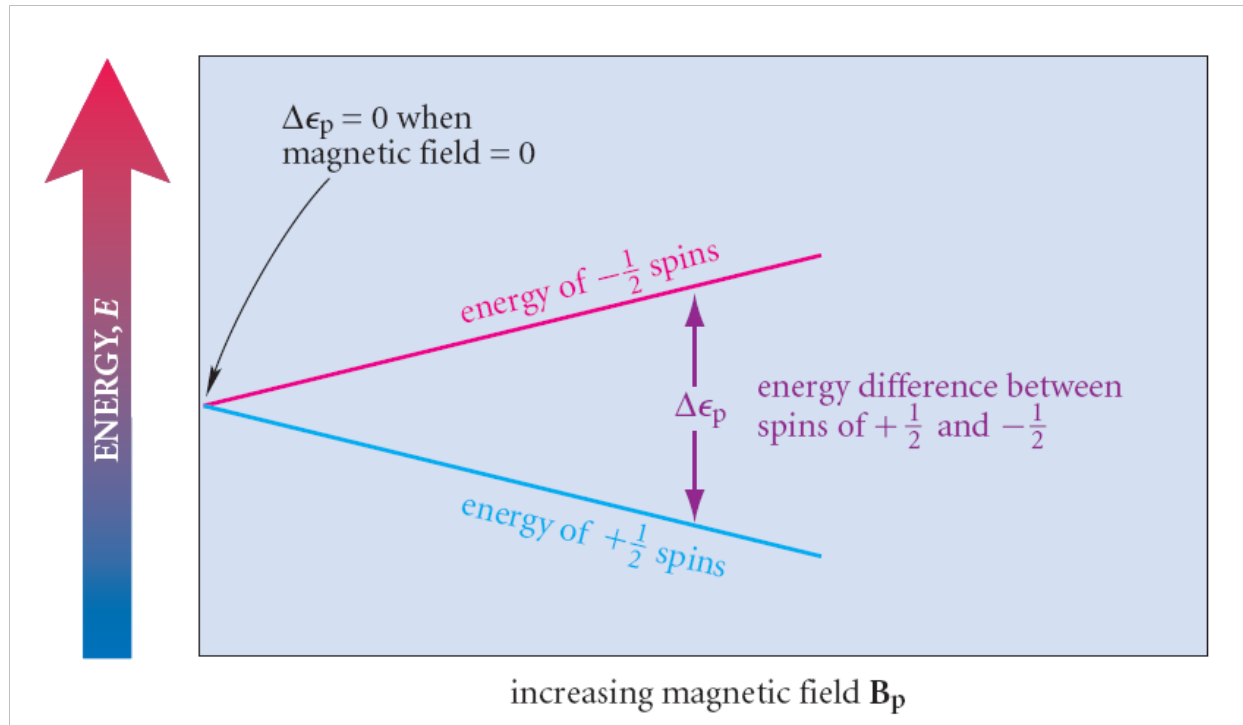
tetramethylsilane (TMS)

Electron alignment by magnetic field



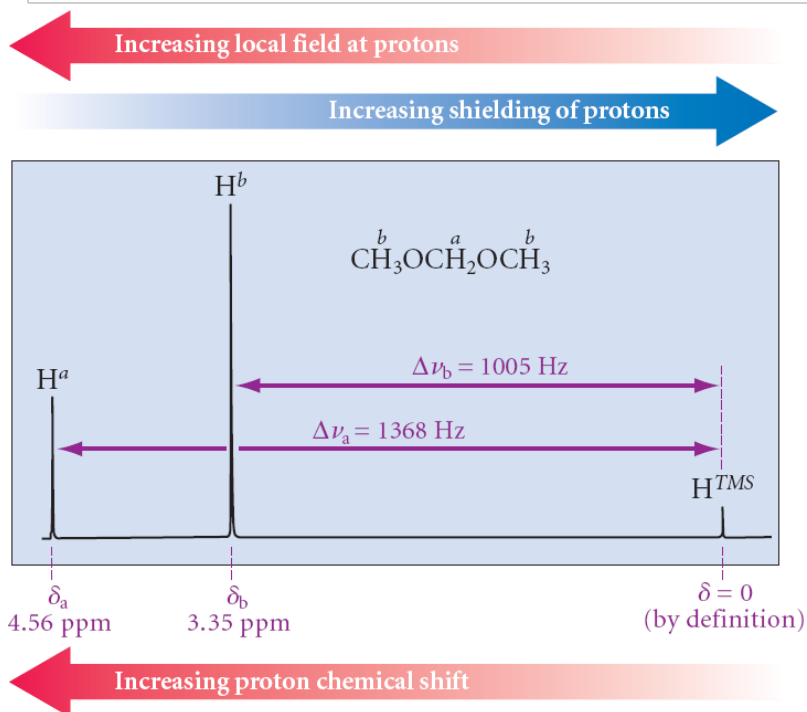
$$\Delta\epsilon_p = \frac{h\gamma_H}{2\pi} \mathbf{B}_p$$

Energy difference upon alignment



Understanding chemical shift

$$\text{radiofrequency required for absorption} = \nu_p = \frac{E_p}{h} = \frac{\Delta\epsilon_p}{h} = \frac{\gamma_H}{2\pi} \mathbf{B}_p$$



$$\mathbf{B}_a > \mathbf{B}_b$$

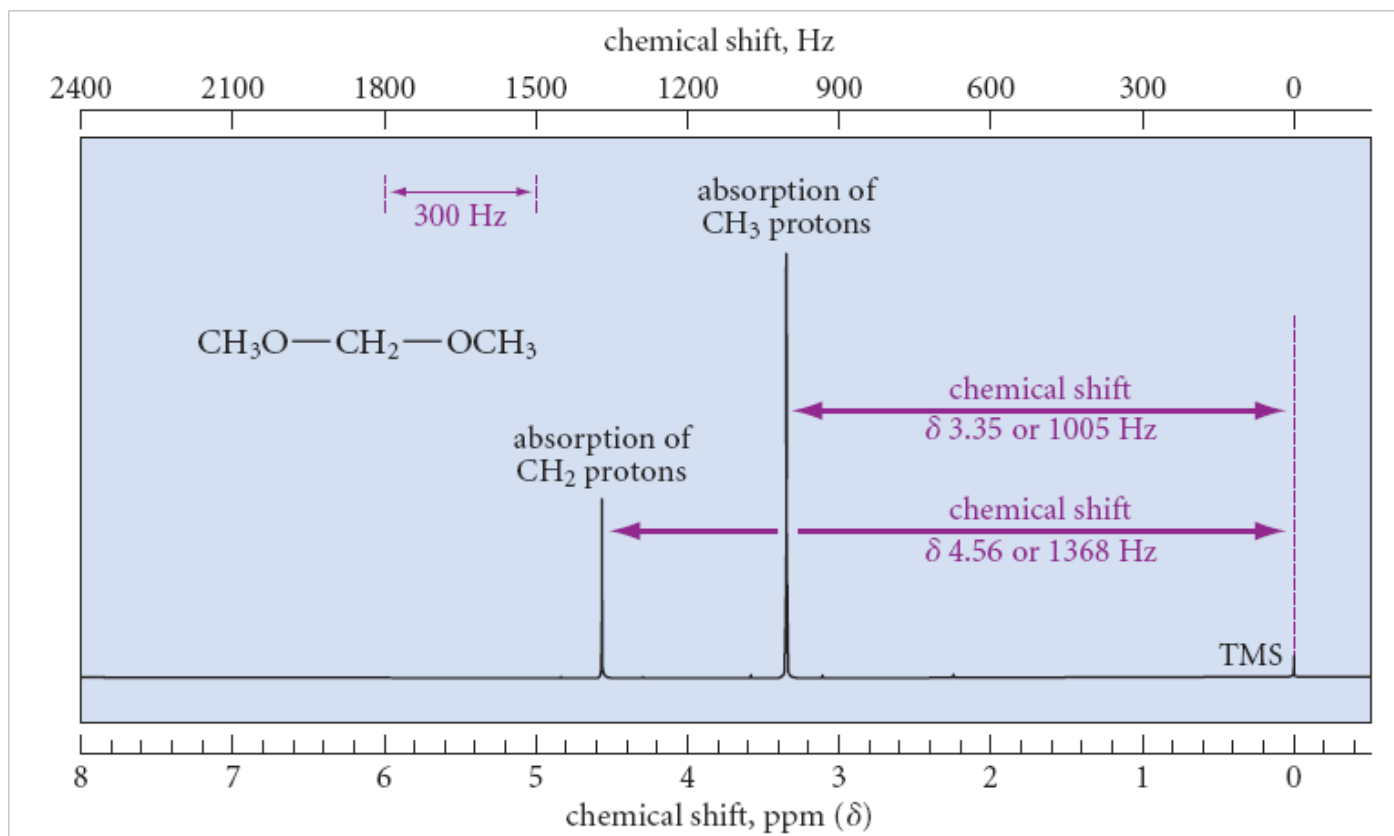
$$\frac{h}{2\pi} \mathbf{B}_a > \frac{h}{2\pi} \mathbf{B}_b$$

$$\nu_a > \nu_b$$

$$\frac{\Delta\nu_a}{\nu_0} > \frac{\Delta\nu_b}{\nu_0} \quad (\Delta\nu \text{ in Hz, } \nu_0 \text{ in MHz})$$

$$\delta_a > \delta_b$$

Units of chemical shifts: ppm



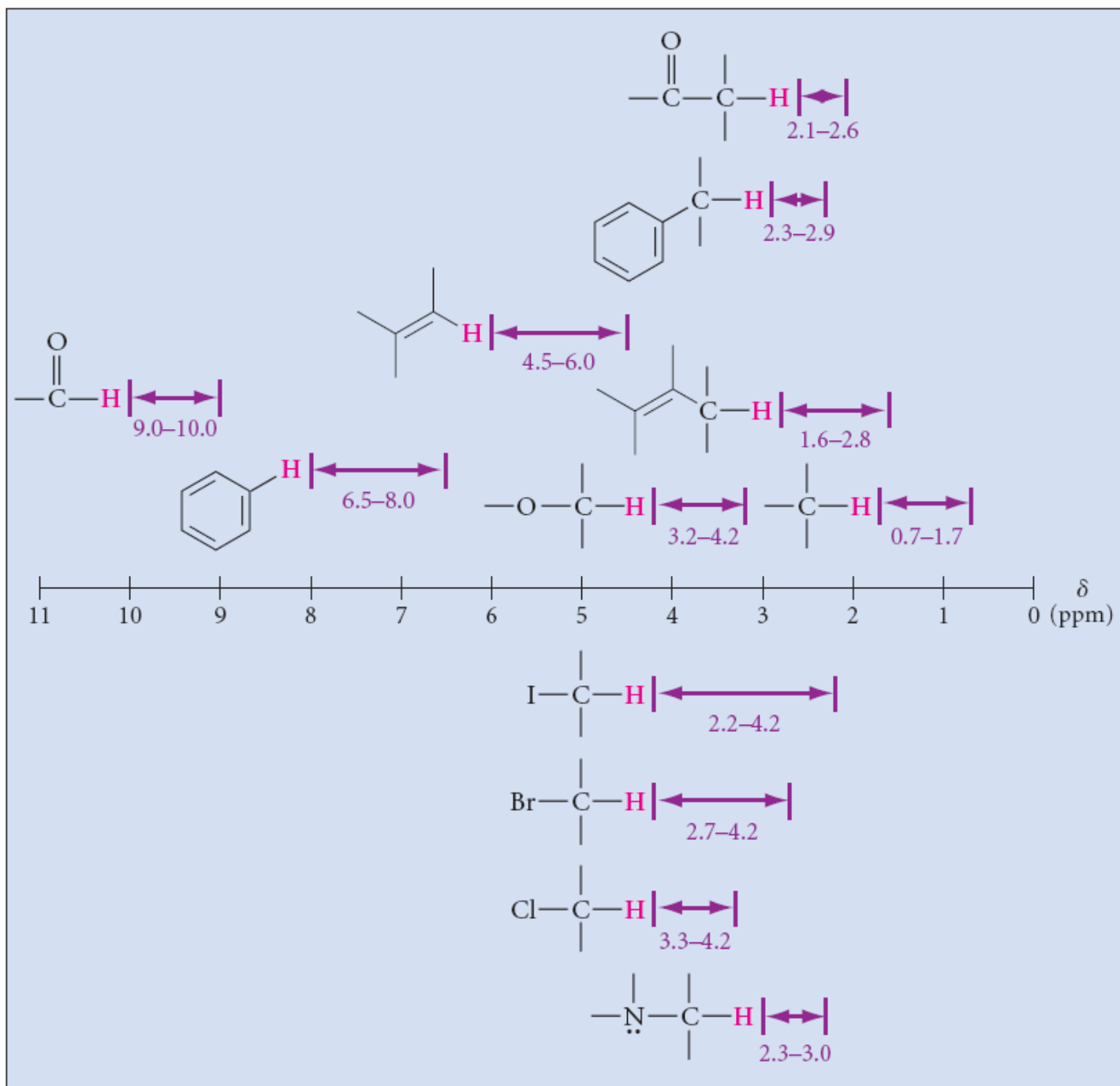
$$\nu_0 = \frac{\gamma_{\text{H}}}{2\pi} \mathbf{B}_0$$

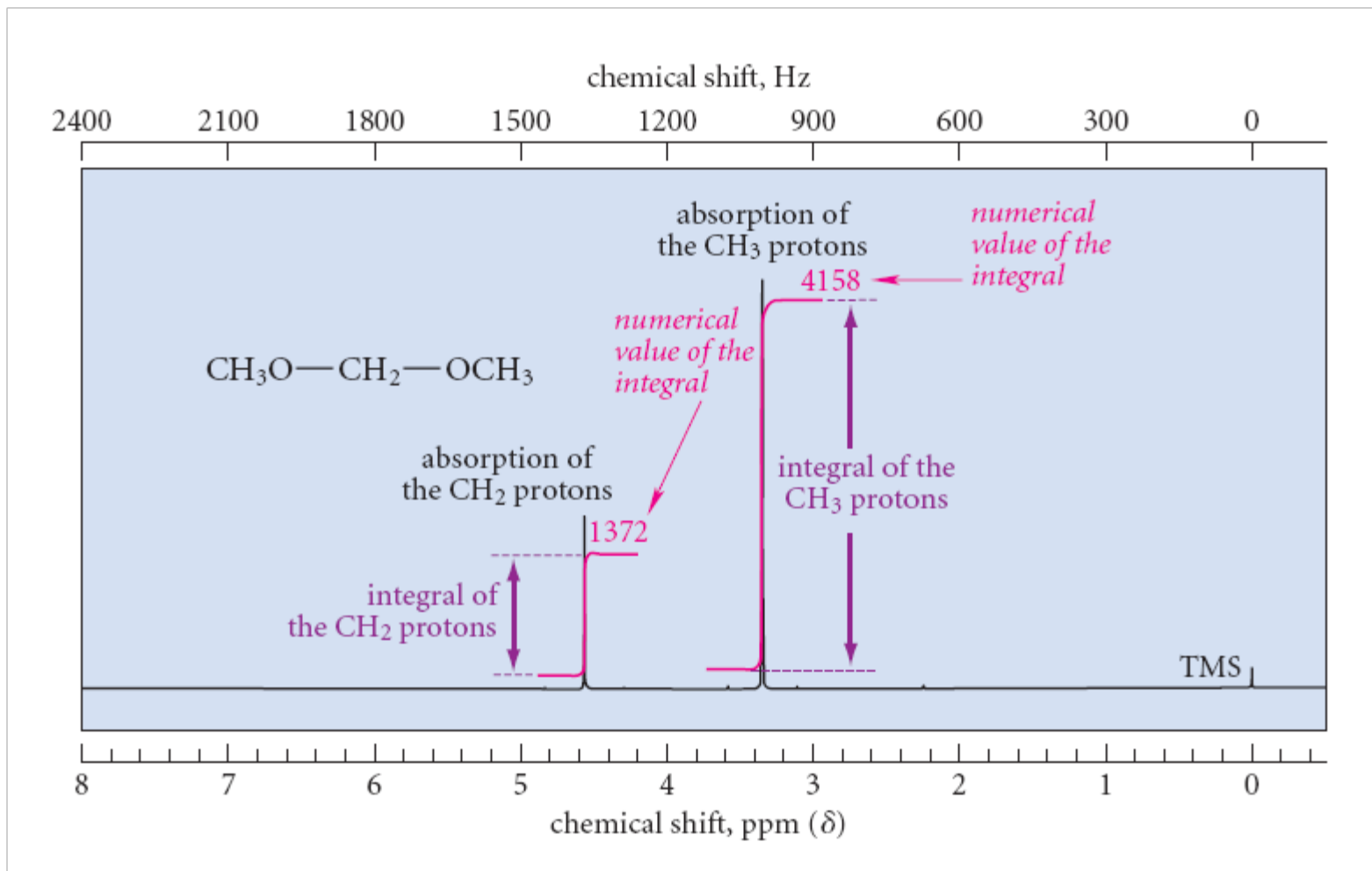
$$\delta = \frac{\Delta\nu}{\nu_0} \quad (\Delta\nu \text{ in Hz, } \nu_0 \text{ in MHz})$$

TABLE 13.1 Effect of Electronegativity on Proton Chemical Shift

Entry number	Compound	Chemical shift, δ	Electronegativity (Table 1.1)
1	CH ₃ F	4.26	F: 3.98
2	CH ₃ Cl	3.05	Cl: 3.16
3	CH ₃ Br	2.68	Br: 2.96
4	CH ₃ I	2.16	I: 2.66
5	CH ₂ Cl ₂	5.30	
6	CHCl ₃	7.27	
7	CH ₃ CCl ₃	2.70	
8	(CH ₃) ₄ C	0.86	C: 2.55
9	(CH ₃) ₄ Si	0.00*	Si: 1.90

*By definition.





Study Problem 13.2: An unknown compound with the molecular formula $\text{C}_5\text{H}_{11}\text{Br}$ has an NMR spectrum consisting of two resonance: one at $\delta=1.02$ (relative integral 8378 units), and the other at $\delta=3.15$ (relative integral 1807 units). Propose a structure for this compound.

n+1 splitting rule

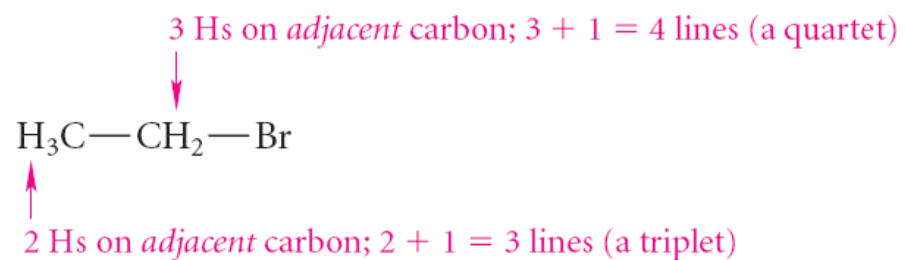
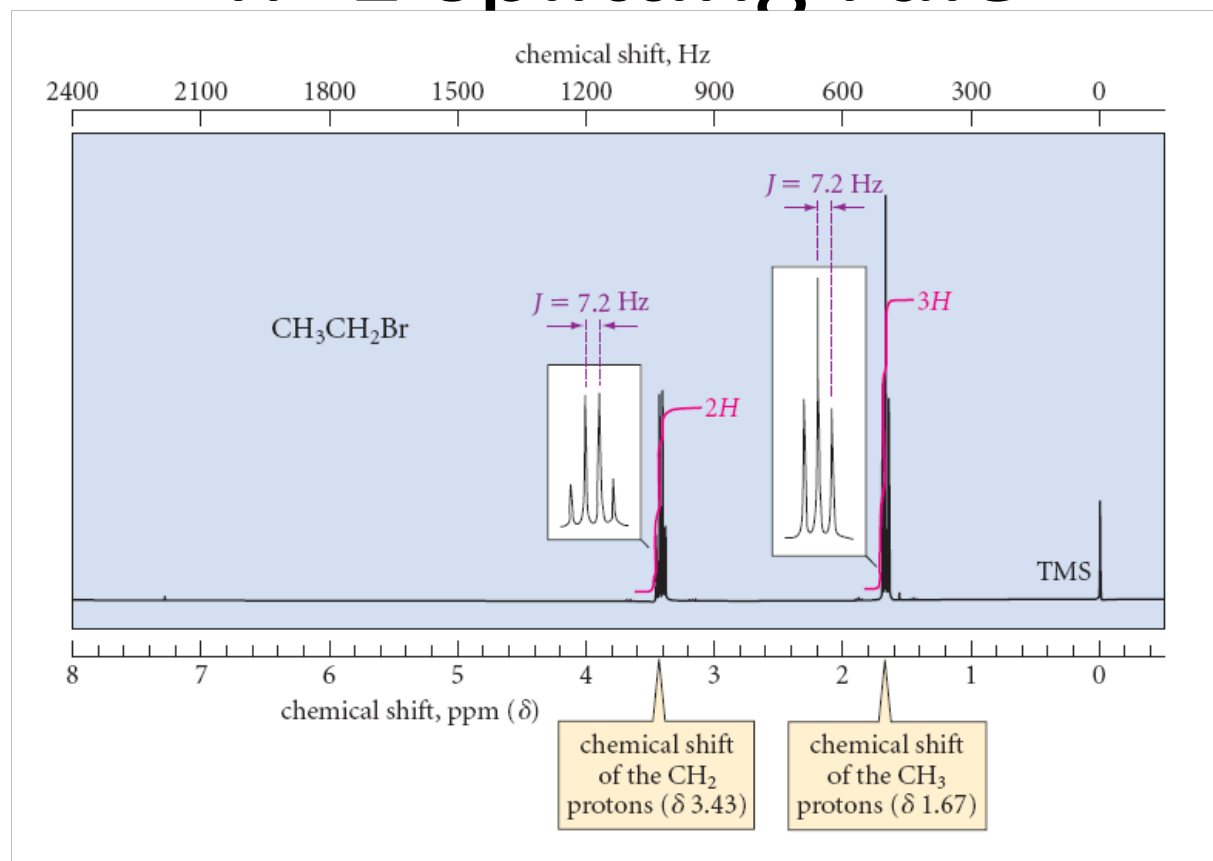
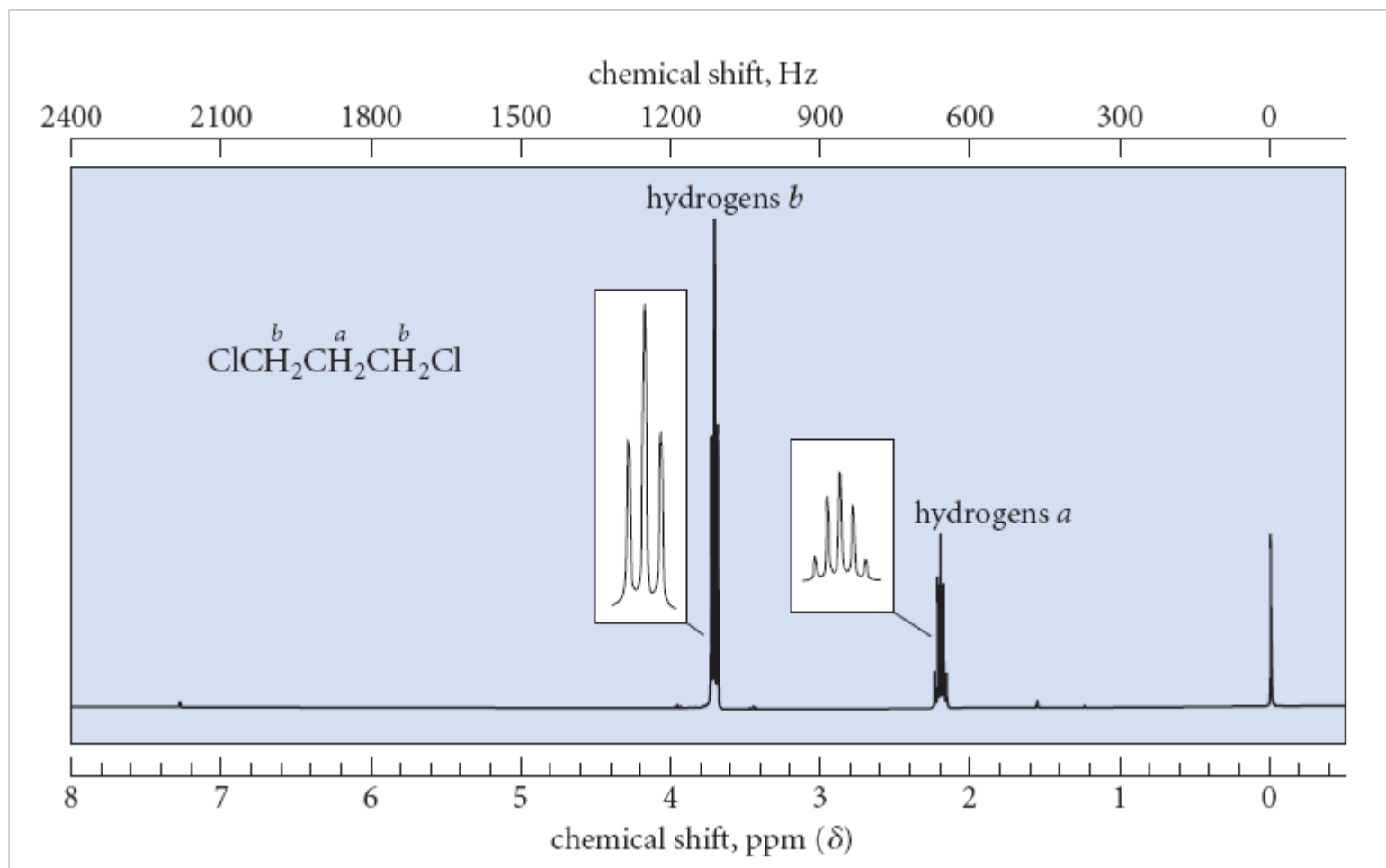
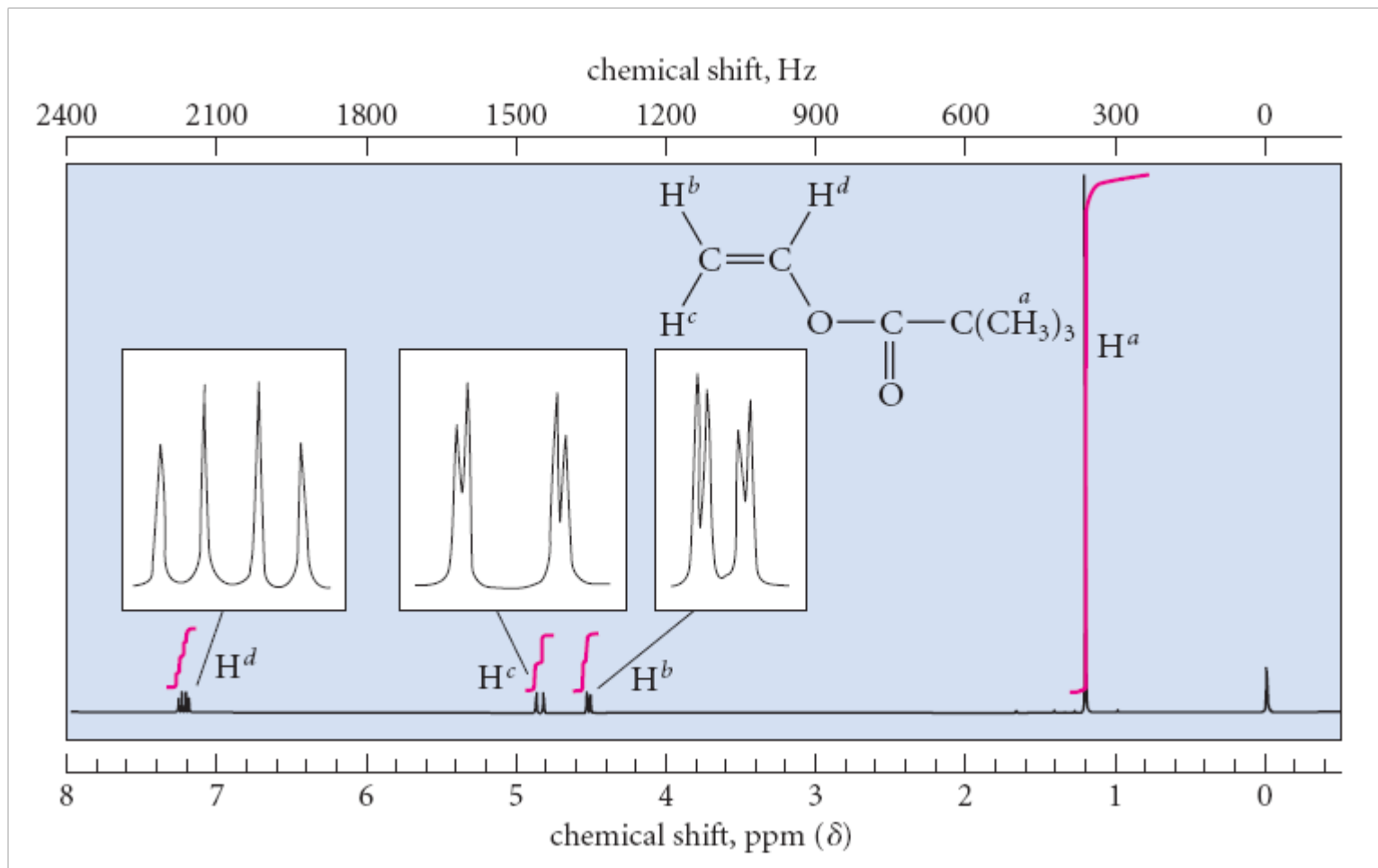


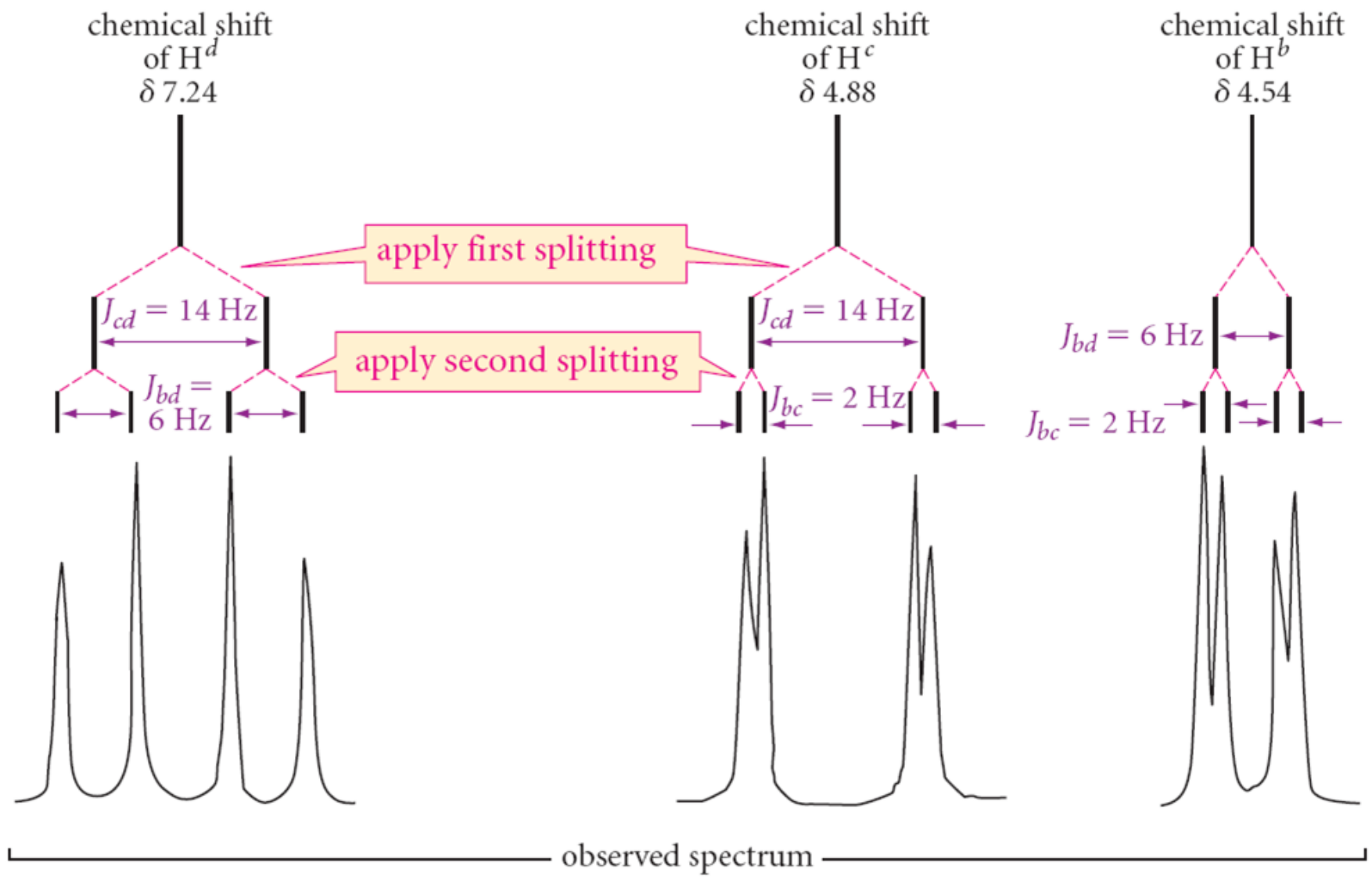
TABLE 13.2 Relative Intensities of Lines within Common NMR Splitting Patterns

Number of equivalent adjacent protons	Number of lines in splitting pattern (name)	Relative line intensity within splitting pattern
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

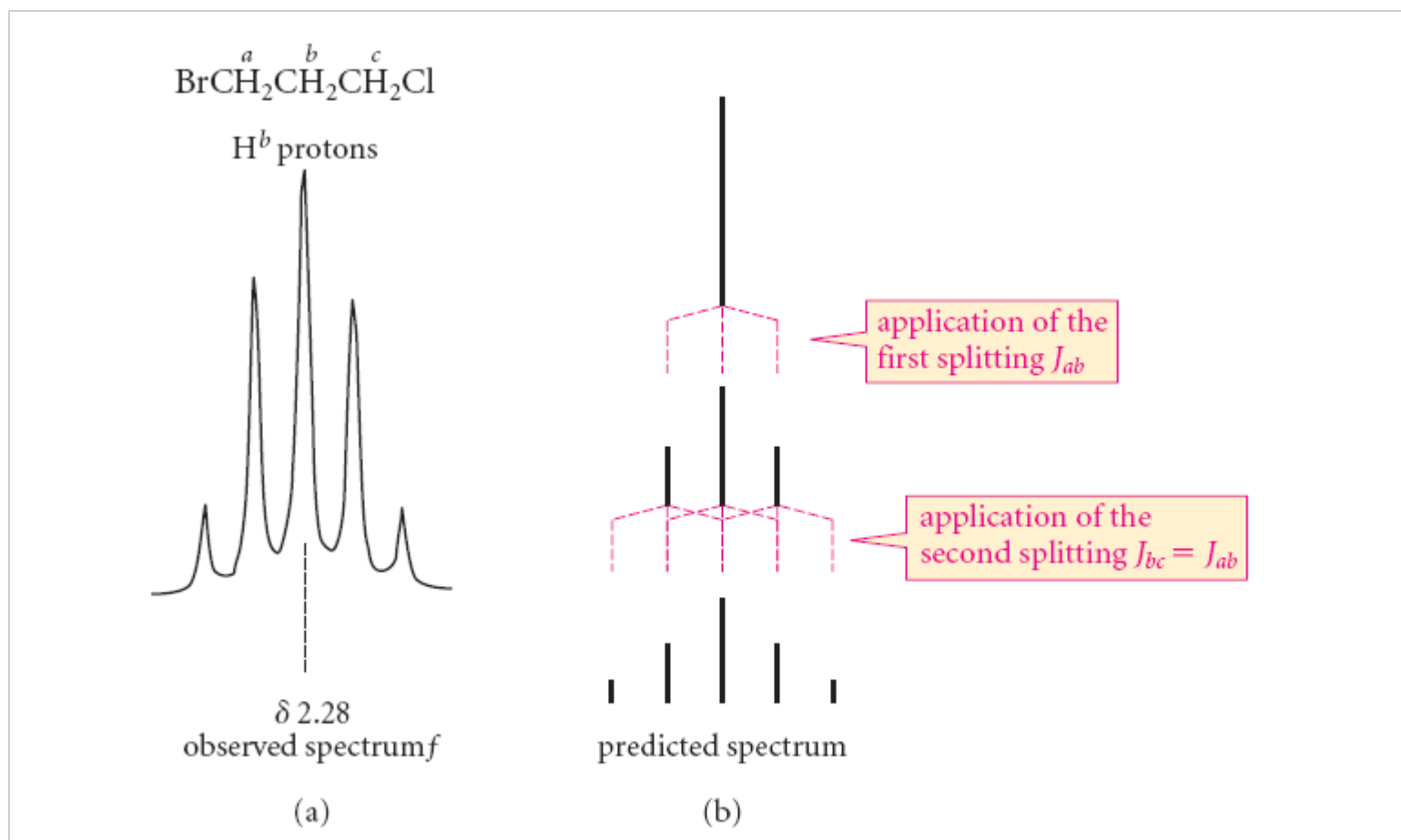


Multiplicative splitting

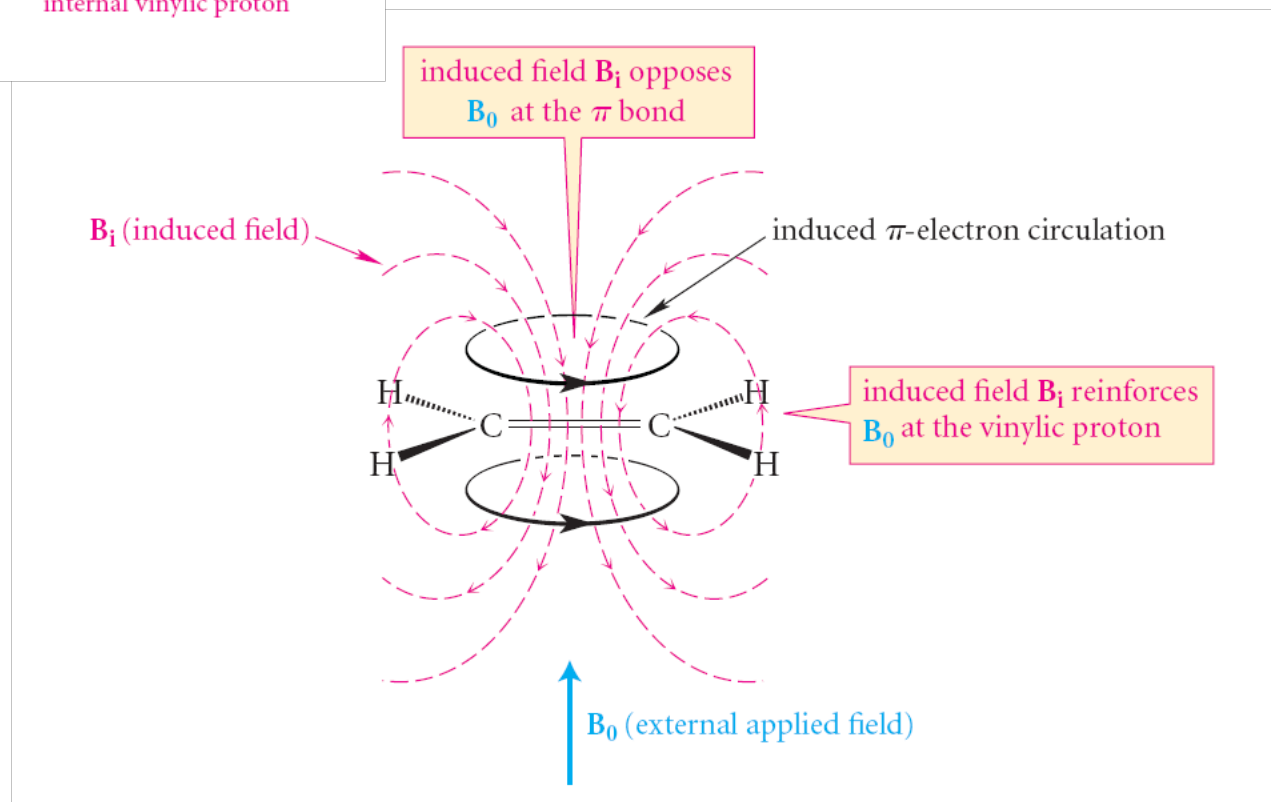
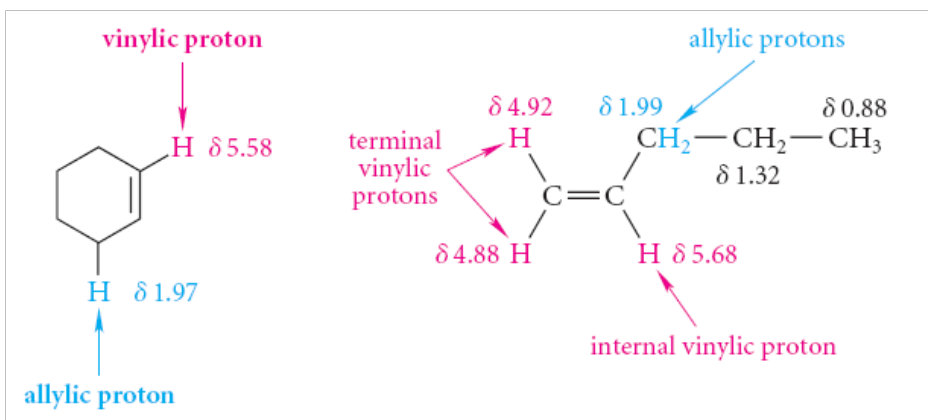




1-bromo-3-chloropropane



NMR of alkenes



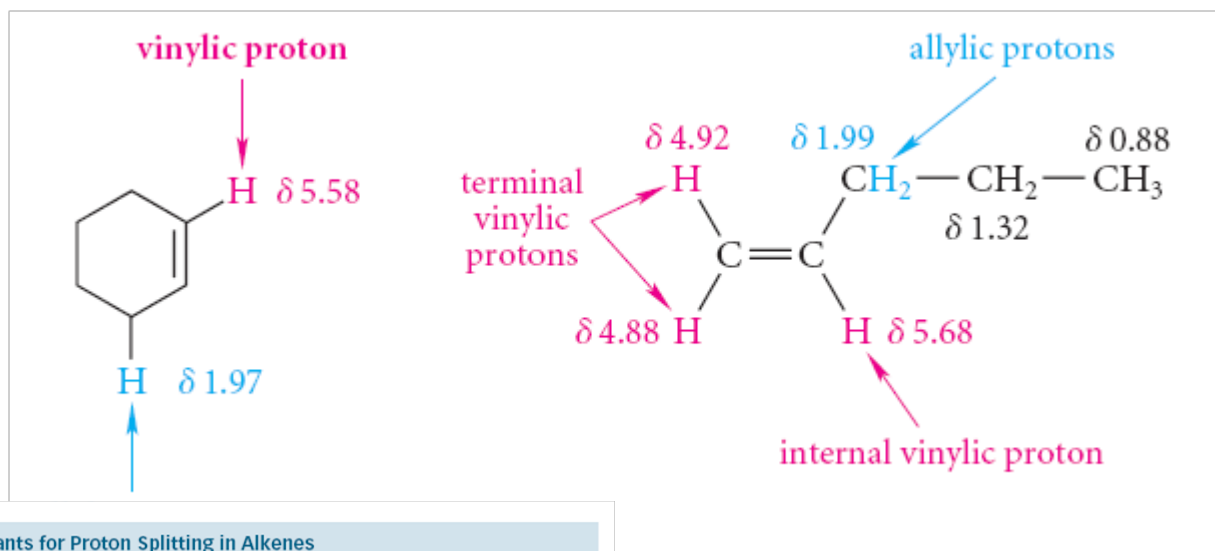
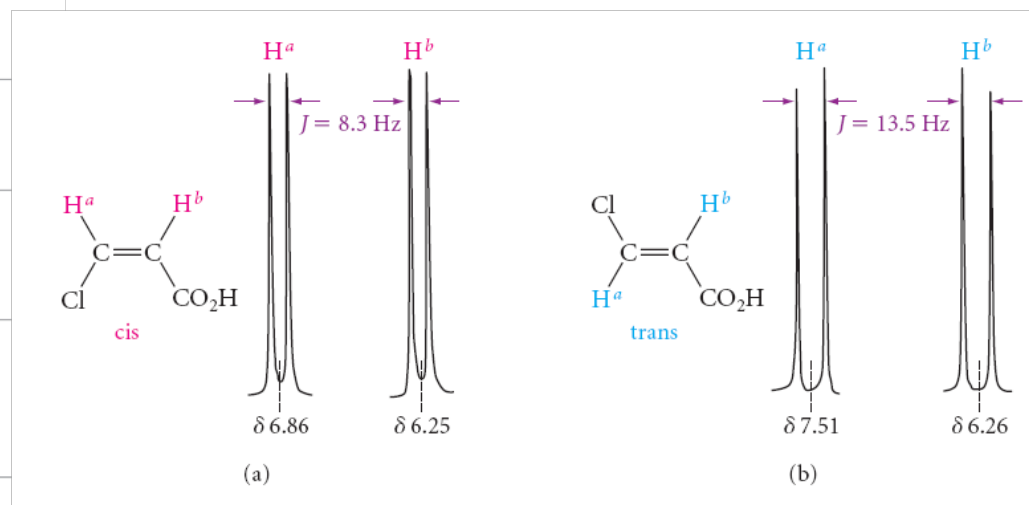
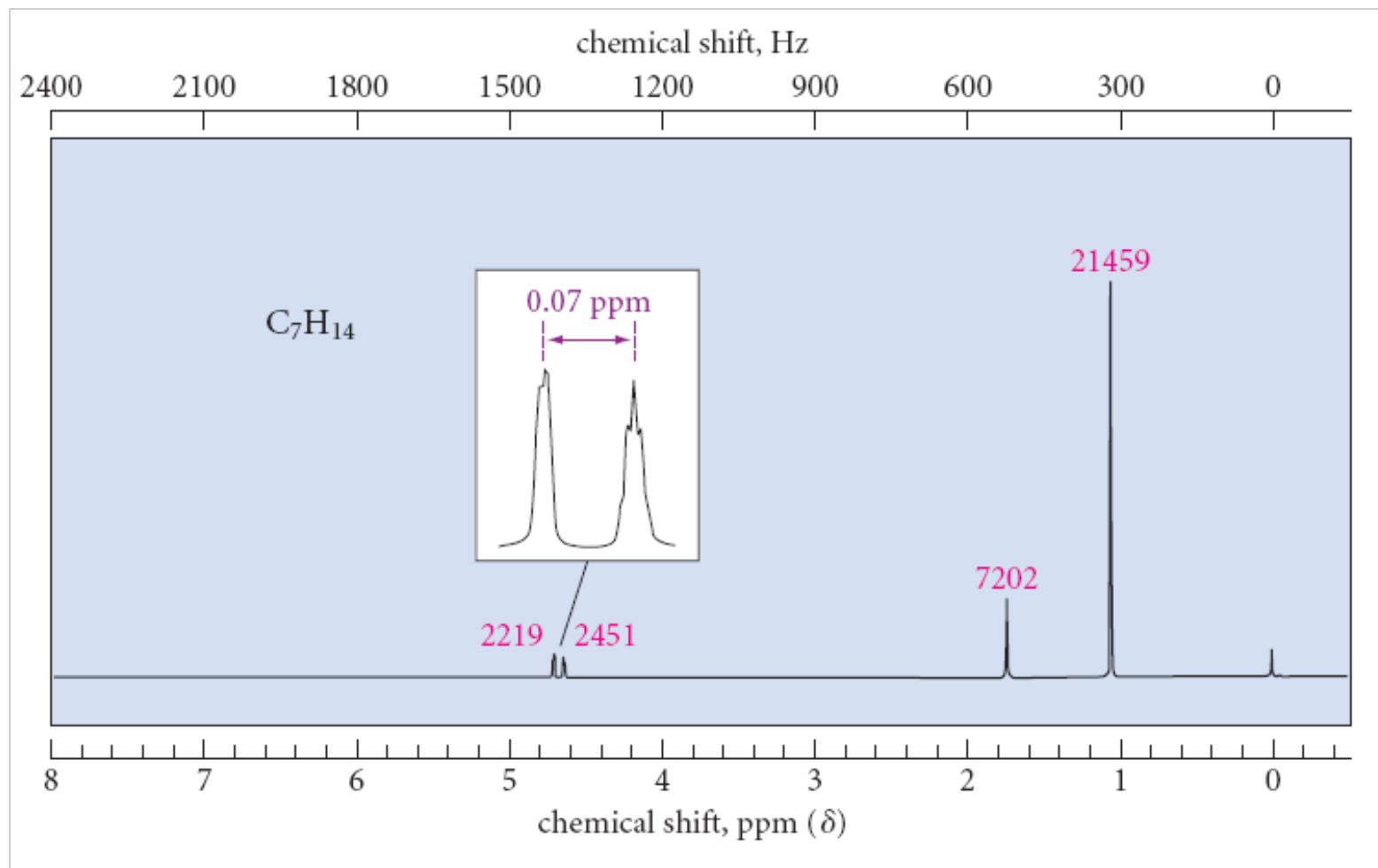


TABLE 13.3 Coupling Constants for Proton Splitting in Alkenes

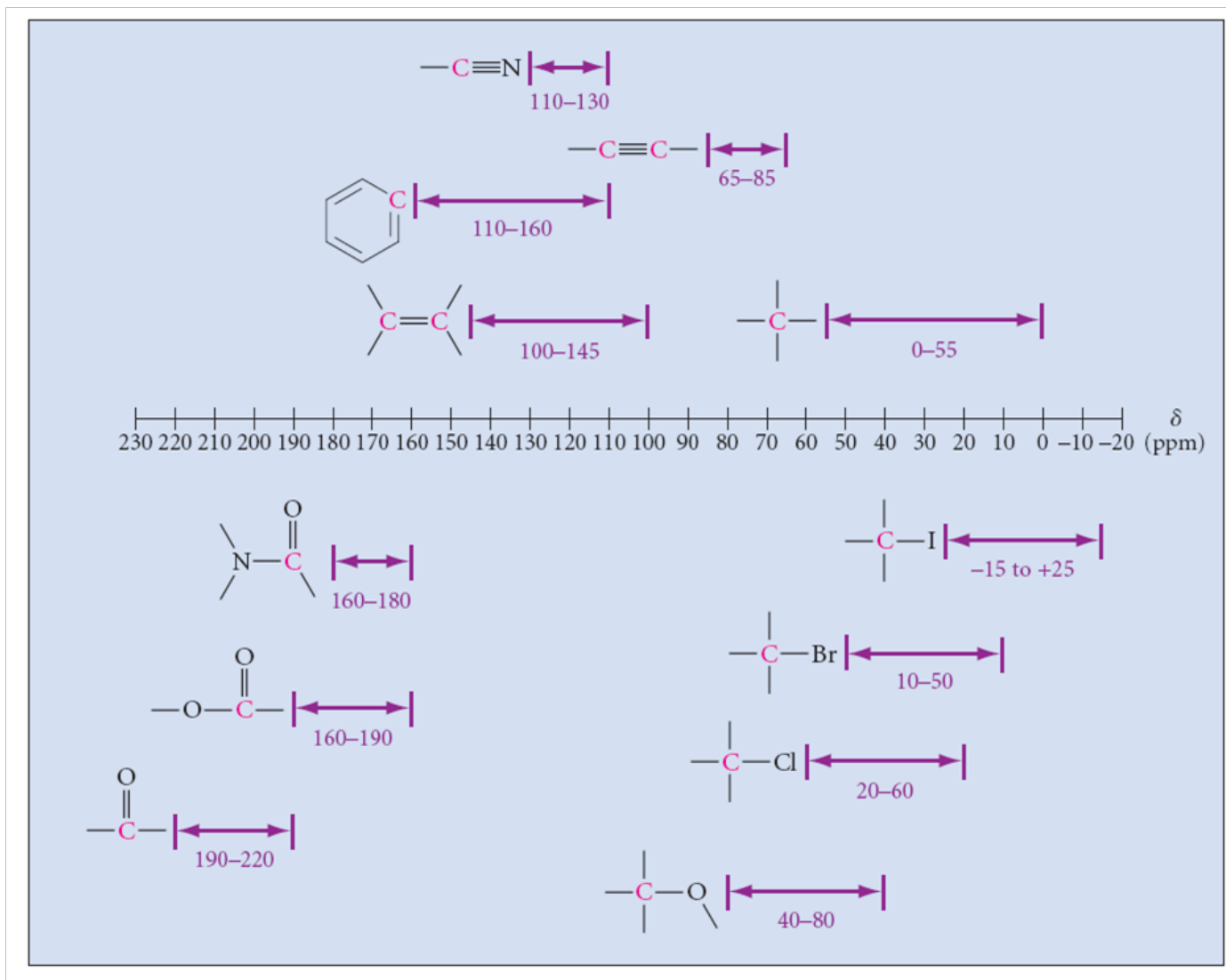
Relationship of protons	Name of relationship	Coupling constant J , Hz
	cis	6–14
	trans	11–18
	geminal	0–3.5
	vicinal	4–10
 (double bond can be cis or trans)	four-bond (allylic)	0–3.0
 (double bond can be cis or trans)	five-bond	0–1.5

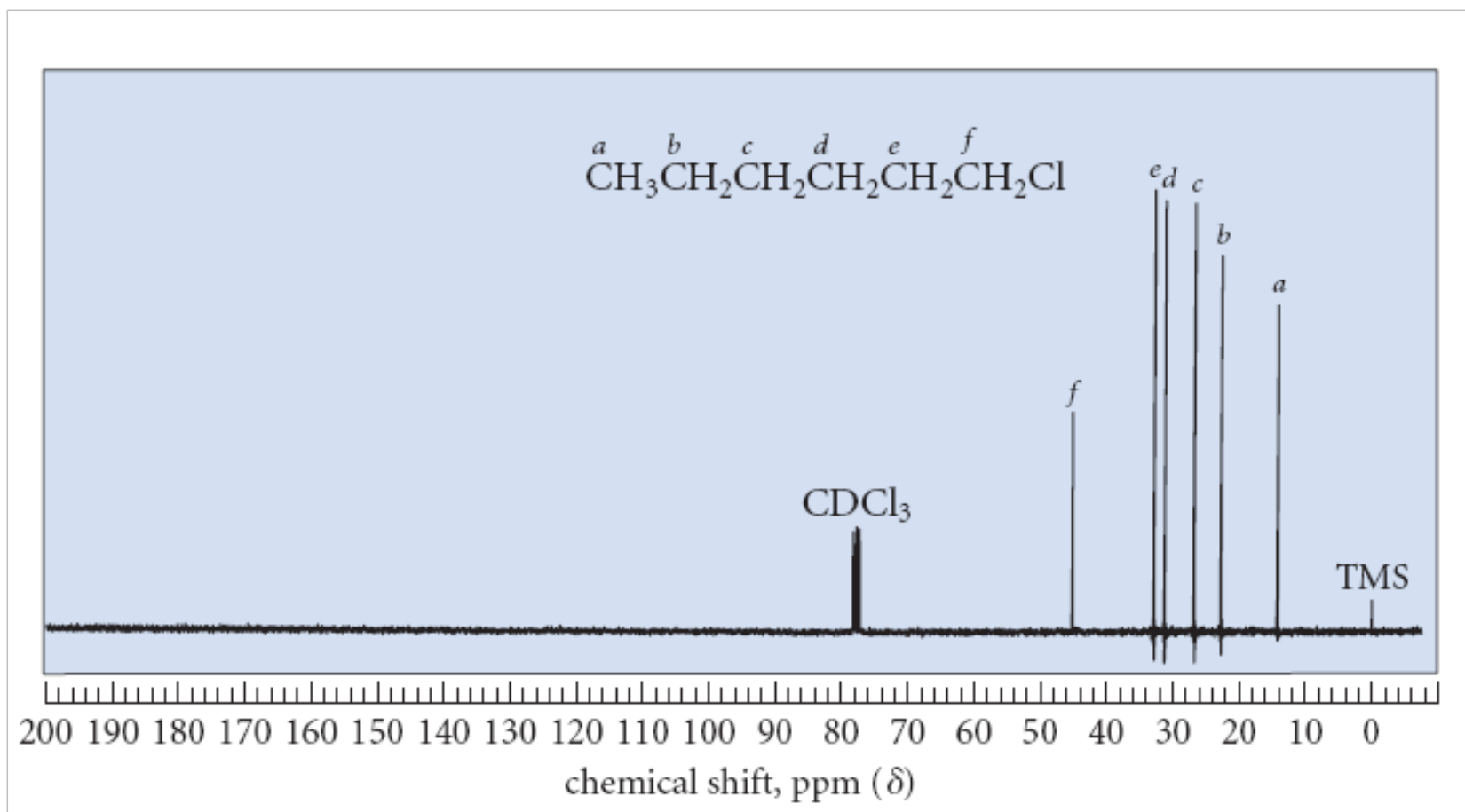


Problem 13.24



Carbon NMR

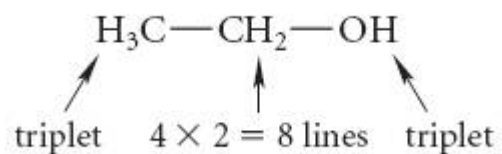




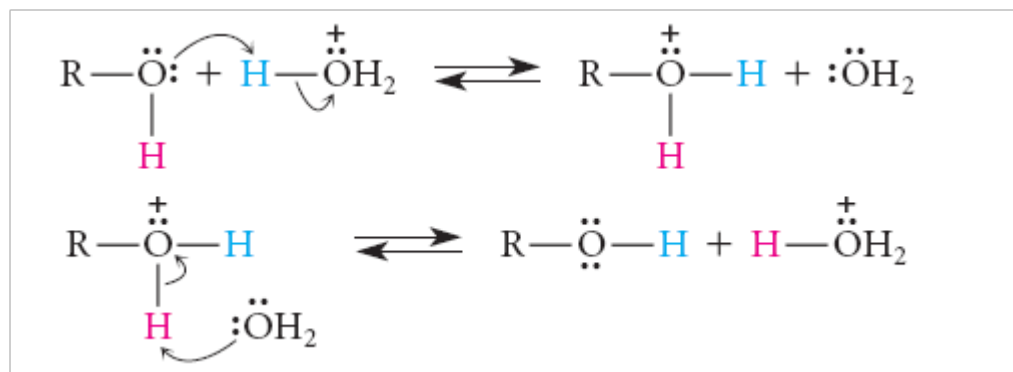
NMR spectra of alcohol



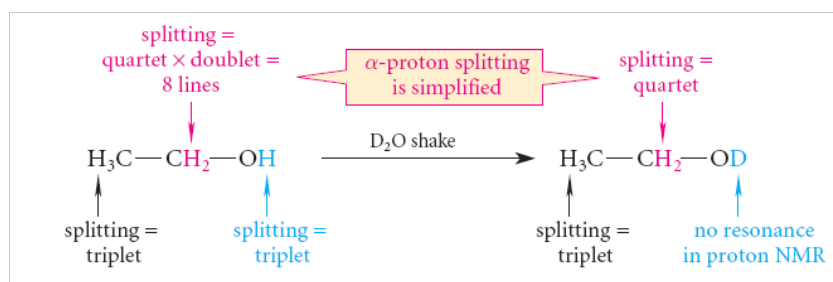
NMR solvents: CCl_4 , CDCl_3 , CD_2Cl_2



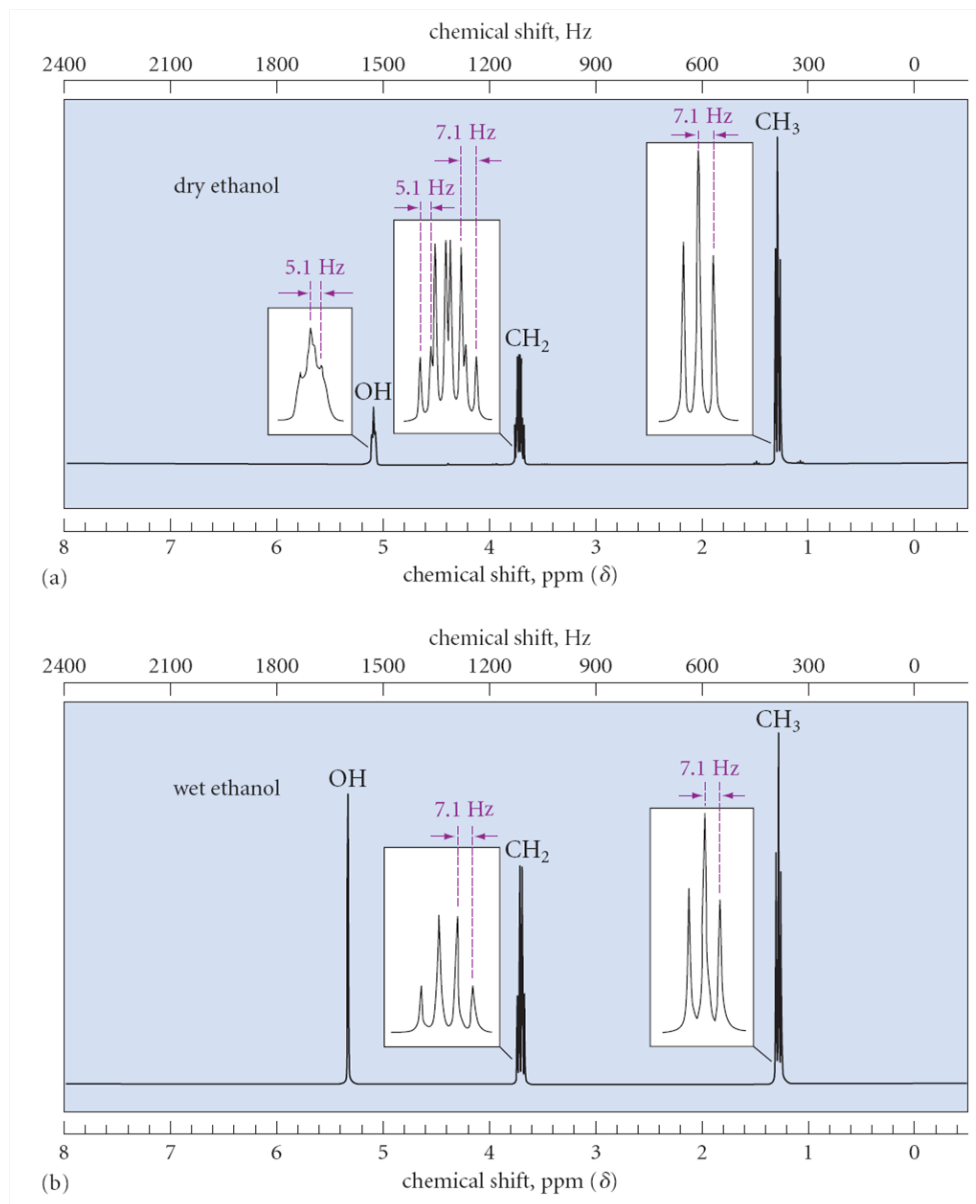
Hydrogen-bonding

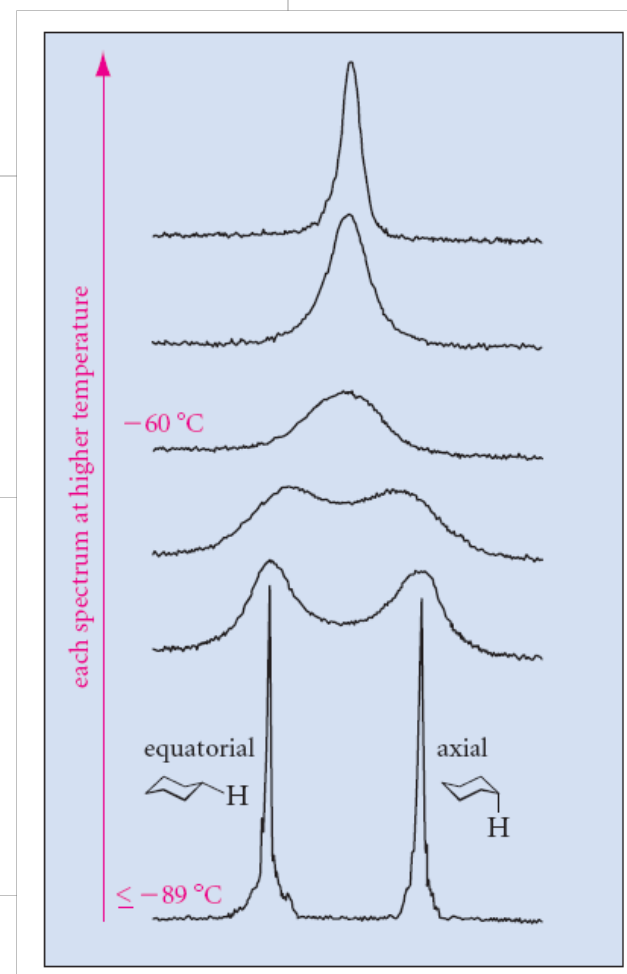
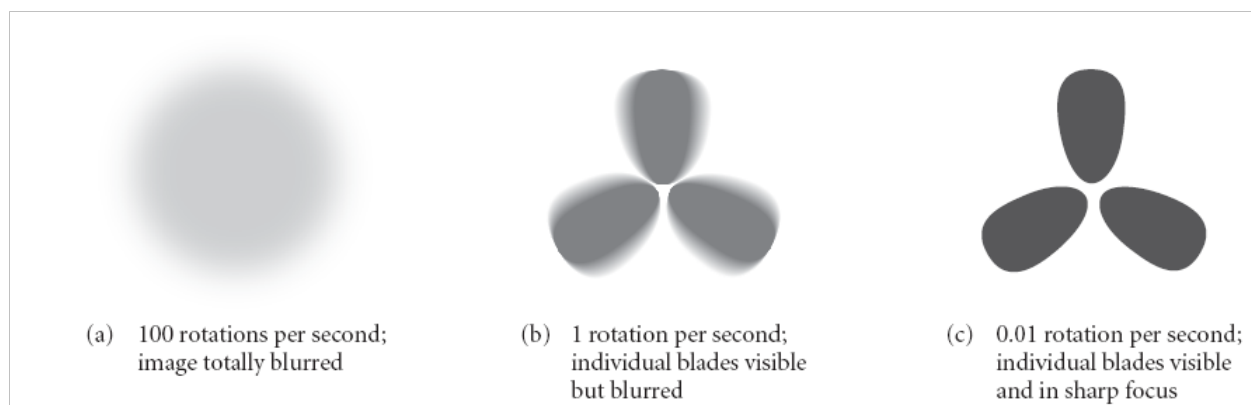
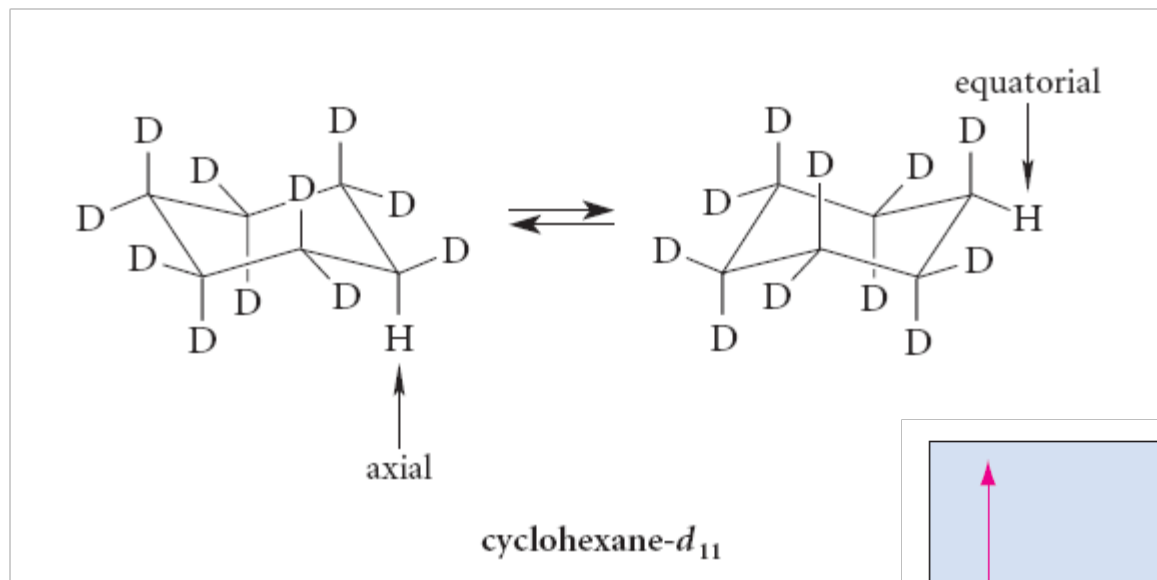


D₂O shake (exchange)

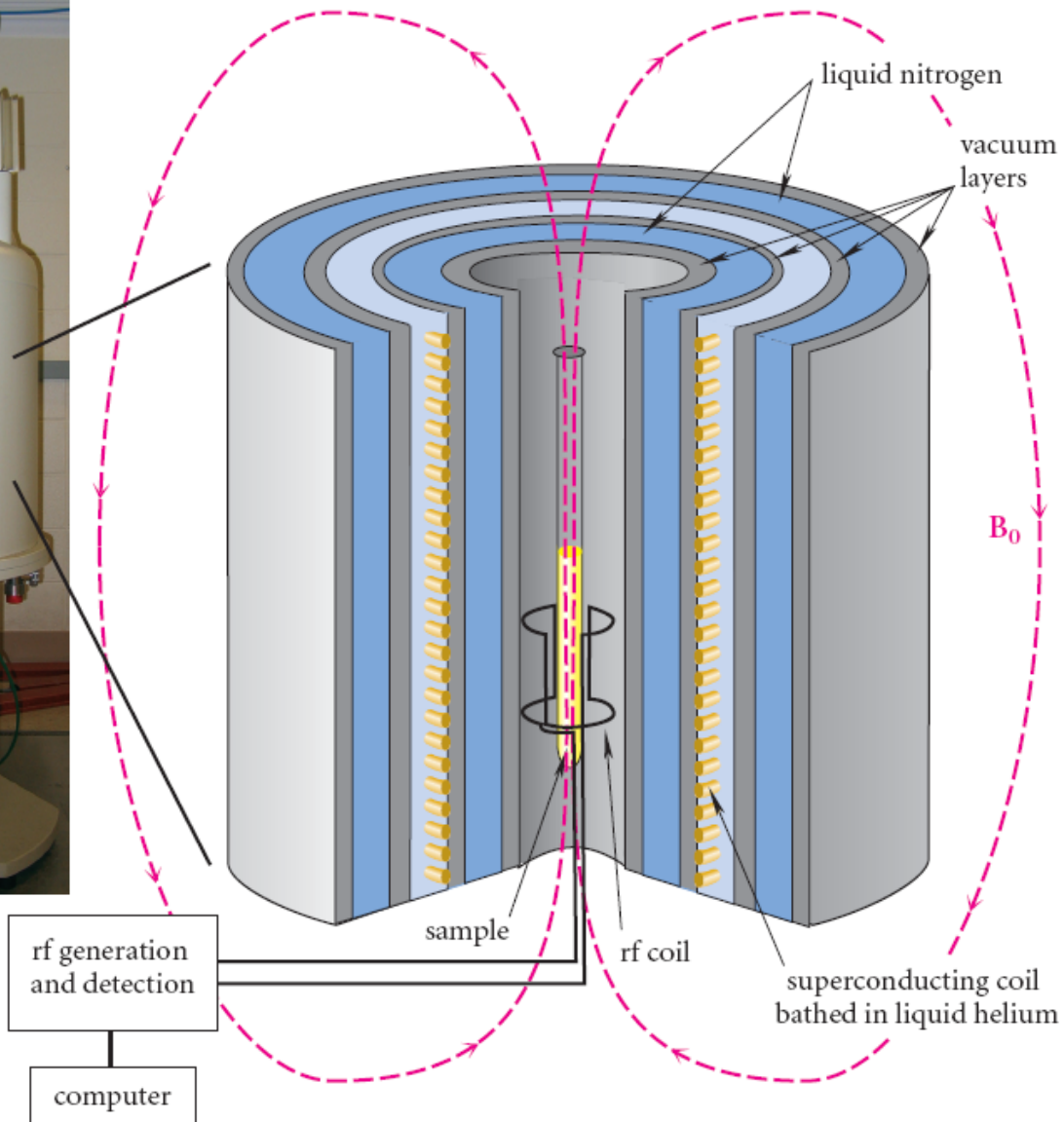


D₂O shake substitutes a hydrogen by deuterium, eliminating its resonance from proton NMR and the splitting that the hydrogen causes.





NMR Spectrometer



Key Points

- NMR basic concept: nuclear magnetic resonance, operating frequency, resonance absorption, chemical shift;
- Physical basis: gyromagnetic ratio, different energy of electrons with different spins;
- Physical basis of chemical shifts and shielding;
- Effects of electronegativity on proton chemical shifts;
- Determination of unknown structures by NMR spectroscopy;
- Spin-spin splitting; analysis of splitting; Information about connectivity;
- $n+1$ rule (exceptions);
- Multiplicative splitting;
- D₂O shake; application of simplifying NMR spectra of alcohols;
- NMR characteristics of alkenes, alkanes and cycloalkanes;
- Carbon NMR.